Theory of colossal magnetoresistance

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Abstract

The history and recent developments in studying (colossal) magnetoresistance in perovskite manganese oxides is reviewed. We emphasize the growing evidence for strongly coupled spin, charge and lattice degrees of freedom. Together with disorder, these provide the microscopic driving forces for local and inhomogeneous textures. The modeling and experimental probes for localized charge–spin–lattice (polaron) structures, and their multiscale ordering, is discussed in terms of a growing synergy of solid state physics and materials science perspectives.

Introduction

It has been known since the early 1950's that manganese oxides, when doped, become ferromagnetic metals, and exhibit remarkable magnetoresistive properties. Zener [1] explained magnetism in these materials via the **d**ouble **e**xchange (DE) mechanism. He assumed that the only way charge transport between Mn^{4+} and Mn^{3+} can happen is via the simultaneous hopping of an e_g–electron from Mn^{3+} to the connecting O^{2-} and from the O^{2-} to the Mn^{4+} e_g band; hence the term double exchange. Ferromagnetism is then induced via this hopping by the very large Hund's rule coupling between the Mn e_g and t_{2g} electrons, resulting from the high spin state of the manganese d–electrons. An explicit formulation of this mechanism was first presented by Anderson and Hasegawa [2], and treated in a mean–field type description by deGennes [3]. In those works, an effective one–band Hamiltonian is proposed which in the limit of infinite Hund's rule coupling reads

$$H_{DE} = -\sum_{ij} \frac{t_{ij}}{\sqrt{2}} \sqrt{1 + \frac{\mathbf{S}_i.\mathbf{S}_j}{S^2}} \left(c_i^\dagger c_j + H.c. \right) \quad , \tag{1}$$

describing the hopping of spinless fermions with a hopping amplitude depending on the relative orientation of the total d–electron spin on neigbouring sites i and j. In early neutron scattering measurements [4] and from magnetic measurements [5] the magnetic and structural phase diagram of $La_{1-x}Ca_xMnO_3$ was mapped out, with little emphasis on the electric properties.

Kubo and Ohata [6] derived a mean field theory for the lanthanate manganites starting from the ferromagnetic Kondo lattice model

$$H_{KLM} = -t \sum_{ij,\sigma} \left(c_{i,\sigma}^\dagger c_{j,\sigma} + H.c. \right) - J_H \sum_{i,\sigma,\sigma'} \left(\mathbf{S}_i.\sigma_{\sigma\sigma'} \right) c_{i,\sigma}^\dagger c_{j,\sigma'} \quad , \tag{2}$$

where spin–$\frac{1}{2}$ e_g–electrons $c^\dagger_{i,\sigma}$ are hopping in a cubic lattice coupled to a local $s = \frac{3}{2}$ spin, describing the three localized t_{2g}–electrons. Kubo and Ohata calculate a magnetic phase diagram, the resistivity and the magnetoresistance. Their results show a ferro– to para–magnetic phase transition at T_c^m, accompanied by a change in the temperature dependence of the resistivity, and a diverging negative magnetoresistance at this transition. However, neither the predicted low–temperature dependence of the resistance ($\approx T^{9/2}$) nor the constant resistivity above T_c^m agree with experiment. In a further paper [7] they also qualitatively discuss the scattering of the charge carriers from temperature induced spin–disorder.

A recent shift of focus onto the magnetoresistive behaviour of the manganates [8] has spawned renewed interest in metallic peroskites $A'_{1-x}A_x\mathrm{Mn\,O_3}$ ($A' = \mathrm{La,Pr,Nd}$, ...,$A = \mathrm{Ca,Sr,Pb}$) as a class, and a new and refined set of data from experiments using modern techniques became available. The term **c**olossal **m**agneto**r**esistance (CMR) was coined to distinguish these materials from the giant magnetoresistive compounds, see e.g. *apo96* and references therein. Typically it is found that at low (high) values of doping x the materials are antiferromagnetic insulators (AFMI) at low temperatures and paramagnetic insulators (PMI) at high temperatures, and at intermediate doping ($0.2 \lesssim x \lesssim 0.4$) a transition from a low–temperature ferromagnetic metal (FMM) to a PMI phase was found. It is in this region that the CMR effect occurs most strongly. A sketch of the phasediagram is shown in Fig. 1. Using a modern version of mean field theory, the $d = \infty$ mean–field theory developed for the treatment of correlated electrons in the high–T_c superconductors, Furukawa [9] reproduced the earlier results of Kubo and Ohata.

In hindsight it appears surprising that little attention was given to the possibility of local lattice or Jahn–Teller distortions of the perovskite unit cells. The importance of a strong electron–coupling in these and related perovskite was well–studied [10, 11, 12, 13, 14], and found to be important for both structural, magnetic and transport properties in perovskites. The inclusion of a coupling of the DE mechanism to the lattice degrees of freedom was argued for by Millis [15] and studied in detail by us [16, 17] and Millis et al [18, 19].

In this short review we will focus on the strong interaction between spin, charge and lattice degrees of freedom with special emphases on the possibility of inhomogeneous, local effects, particularily charge localization, (small) polaron formation and ordering. We believe those are the driving force for many of the exciting phenomena exhibited by the CMR perovskites, especially the formation of charge and spin–ordered superlattices, the unusual magnetostrictive behaviour, first order structural phase transitions driven by a magnetic field, etc. In the next section we gather the experimental evidence for polaronic behaviour, mostly above T_c^m, followed by a discussion of the measurements of local structure and their relation to macroscopically ordered phases. Then we describe the theoretical models and techniques used to include lattice effects in an averaged way, and their possible modifications and extensions to include local effects, in spin, charge and lattice. We conclude with a summary of some probable future focal areas of research in the CMRs.

Polarons in CMR

That polarons play an important role in the charge transport of the CMR perovskites, at least in the insulating phase above T_c^m and the MI transition, is obvious from the activated behaviour of the conductivity. In addition, a coupling of the transport to lattice degrees of freedom is also evident from the magnetostriction and magnetoelastic

effects observed by Ibarra et al [20] in $La_{0.6}Y_{0.07}Ca_{0.33}MnO_3$. Below a temperature $T_p = 320K$ they find a deviation of the magnetostriction $\Delta l/l$ from normal behaviour down to T_c^m where $\Delta l/l$ drops to a lower value. In this regime the magnetostriction is isotropic. Ibarra et al interpret this as the region where "large" polarons start to form. The FMM phase is the low volume phase and shows anisotropic magnetostriction comparable to normal d–metals. Even below T_c there is evidence for at least spin–polaronic behaviour. From a careful study of resistivity ρ versus magnetization m in $(La_{1-x}Y_x)_{2/3}Ca_{1/3}MnO_3$. Hundley et al [21] Martinez et al [22] find the dependence $\rho \propto \rho_m \exp(-m(h,t)/m_0)$. This means that transport even in the FMM is controlled by magnetic polarons. Martinez et al interpret the localization of charge carriers above T_c as being due to scattering of these magnetic polarons on the magnetic disorder above T_c. However, it is certain that the lattice is involved in the charge–localization, and we believe that the lattice dynamics predominantly slaves the charge and spin dynamics and not vice versa.

The existence of small polarons above T_c has been established by a variety of transport measurements. For example the high temperature thermopower exhibits typical polaronic behaviour [23, 24, 25, 26]. The deduced activation energies fit well with the ones obtained from Hall effect measurements [27]. As T approaches T_c both the activation energies for the resistivity and the thermopower become dependent on a magnetic field showing the additional magnetic character of these polarons. Jaime et al [23] therefore use the term "magnetoelastic polarons" to describe the carriers just above T_c.

In addition to the above indirect evidence for the relevance of polarons in the CMRs drawn from transport measurements there is now direct evidence. Using electron paramagnetic resonance (EPR), which measures the local magnetic response, Oseroff et al [28] found activated behaviour in the EPR resonance for $T > T_c^m$ in $La_{1-x}Ca_xMnO_{3+\delta}$. Already below about $T \lesssim 600K$ they find deviations from standard Curie–Weiß behaviour. At temperatures $20K$ above T_c^m they deduce an effective spin of about 30. This means that about seven manganese are involved in the magnetic character of the magnetoelastic polaron. This agrees well with our unrestricted mean–field calculation of the spin character of local polarons above T_c [16]. The additional influence of lattice degrees of freedom was directly observed in the EPR measurements of Shengelaya et al [29] who studied the influence of oxygen isotopic substitution ($^{16}O/^{18}O$) on the EPR resonance. Shengelaya et al calculated the strength of the DE induced ferromagnetic interaction J between Mn^{3+} and Mn^{4+} from the temperature dependence of the EPR signal. They found J to depend on the oxygen mass, which strongly indicates that spin–lattice coupling is important , and indirectly means that local charge transfer also depends on the lattice since magnetism is induced by local hopping.

Direct measurements of the oxygen displacements are presented by Sharma et al [30] from ion channeling (IC) experiments in $Nd_{0.7}Sr_{0.3}MnO_3$, $Pr_{0.7}Ba_{0.3}MnO_3$, and $La_{0.7}Ba_{0.3}MnO_3$. IC is a direct real space probe of very small ($\approx 1pm$) displacements u of atoms from their regular positions. Sharma et al find a very strong correlation of the resistivity with $\frac{du}{dT}$, indicating that transport is strongly correlated with **local** lattice distortions. As the temperature is lowered from the PMI to the FMM phase the measured distortion decreases and reaches a steady state below T_c. Both the Mn and to a lesser degree the rare earth sites are involved.

Summarizing these experimental results, we believe that magnetoelastic polarons dominate transport above T_c. As T approaches T_c from above, the magnetic component of these composite particles becomes spatially extended, and eventually leads to a delocalization of charge and spin degrees of freedom in the FMM phase.

Local structure measurements, polaron lattices and charge ordering

The experimental evidence for spatially inhomogeneous behavior in CMR materials has begun to grow rapidly both in more conventional global signatures (e. g. optics and thermodynamic properties, such as specific heat, by magnetotransport measurements, Hall effect measurements, even within powder neutron measurements[31]) and. most strikingly in more local probes. The latter include neutron pair–distribution function (PDF)analysis [32, 33], extended x–ray fine structure (XAFS) [34], μSR [35], XAS and ARPES [36], measurements of the isotope effect [37], perturbed angular correlation spectroscopy [38], and high–resolution electron microscopy HREM [39]. The availability of the local probes is in many cases rather new and for the first time opens the possibility of systematically exploring the interrelated reflections of multiscale structure and dynamics in complex electronic materials such as transition metal perovskites. As we have emphasized, in those materials, the multiscale patterns may well have major intrinsic components and be driven at a microscopic level by strong coupling of spin, charge and lattice degrees–of–freedom. The signatures of mesoscopic multiscale patterns must then be measured in each of these degrees of freedom and shown to be self–consistent with each other to establish a valid microscopic model, and permit reliable predictions of macroscopic functionalities. While we are at the beginning of this systematic exploration of transition metal perovskites (and other complex electronic materials), some important recent results in CMR materials are already available. In particular the resolution of fine–scale lattice structures and their relation to charge (polaron)–localization and ordering represents a quite new merging of traditional solid state and materials science perspectives, and is gradually being augmented by electronic structure and magnetic signatures.

For example, Ramirez et al. [40] report thermodynamic and electron diffraction signatures of charge– and spin–ordering in $La_{1-x}Ca_xMnO_3$ around $x \approx 2/3$, where strong lattice commensurability can stabilize a near–perfect superlattice ordering. They infer (from specific heat and electron diffraction) charge–ordering at $T_c \approx 260K$ accompanied by a large ($> 10\%$) increase in the sound velocity, implying a significant electron–lattice coupling. More direct elastic constant measurements are certainly needed for specific assignments of structural distortions.

An alternate regime of (hole) charge–ordering occurs for $x \lesssim 0.5$ in $Pr_{1-x}\,Ca_xMnO_3$. This has been studied intensively by Tomioka et al [41] taking additional advantage of tuning via a magnetic field, and by Lees et al [42] in less detail but over a wider concentration regime. On the basis of resistivity measurements Tomioka et al suggest a real–space ordering at $T_c \approx 230K$ of $1:1$ $Mn^{3+}:Mn^{4+}$ species optimized around the $x = \frac{1}{2}$ commensurate doping with discommensurations growing in for $x < \frac{1}{2}$, weakening the insulating charge–ordered state and eventually melting it (in a strong enough magnetic field). This melting is controlled by an external magnetic field and a x–H–T phase diagram is mapped out by Tomioka et al [41] Since the conduction electrons (polarons) are unusually strongly coupled to the local spins (via the DE effect), the resistive state is strongly affected by the local spin configuration. Similar charge–orderings occurs in $La_{1-x}Ca_xMnO_3$ [43, 44], $Pr_{1-x}\,Sr_xMnO_3$ [41], $(Nd,Sm)_{1/2}Sr_{1/2}MnO_3$ [45], and $Nd_{1-x}Sr_xMnO_3$ [46] but are more confined to the near–commensurate $x = 1/2$ doping. $La_{1/2}Ca_{1/2}MnO_3$ is distinctive since it shows at least four, with respect to spin– and charge–distribution, phases as a function of magnetic field [43]. It is likely that the special role of $Pr_{1-x}\,Ca_xMnO_3$ is controled by the similarity in ion radius of Pr^{3+} and Ca^{2+}, which gives rise to less cation in-

duced lattice disorder [47] and hence enables the observation of a variety of charge and spin ordered phases. The charge ordering in $Pr_{1-x}\,Ca_xMn\,O_3$ is accompanied [48] by a change in the average lattice parameters of 0.6 – 2.4% followed by antiferromagnetic and canted antiferromagnetic ordering at lower temperatures. Teresa et al [48] have recently reported evidence for charge localization (in the form of a small polaron) in $Pr_{2/3}\,Ca_{1/3}Mn\,O_3$ for $T_p \lesssim 400K$ which, however, only charge–orders below $T_c \lesssim 210K$. They report thermal expansion and magnetostriction measurements (up to 14 T). A continuous change in volume is measured for $T_c < T < T_p$, and the magnetic field suppresses charge–ordering below T_c giving rise to a first–order structural transition. The electrical behaviour is similar to the structural behaviour, again supporting a spin–charge–lattice coupling.

Evidence for coupled lattice and magnetic effects have been reported by Argyriou et al [49] in $La_{0.875}Ca_{0.125}Mn\,O_{3+\delta}$, following earlier reports of a discontinuous volume contraction of the lattice ($\Delta V/V \approx 0.1\%$) at the ferromagnetic transition temperature. Based on powder neutron and Rietveld analysis, Argyriou et al suggest that as T is lowered below room temperature there is a a rapid development of a large breathing–mode (oxygen) distortion coinciding with large positive and negative expansions of the c and b axes, respectively. Canted ferromagnetic ordering onsets at $\approx 220K$ correlated with the reduction of the (averaged) breathing distortion. Similar effects were reported by Kawano et al [50] in $La_{1-x}Sr_xMn\,O_3$ ($x < .17$), who discuss these effects in crystallographic terms. However, the maximum shift of the scattering peaks at $x = \frac{1}{8}$ makes a discussion in terms of an ordered polaron superlattice more appropriate. Indeed in the same material Yamada et al [51] find a polaron lattice at $x = \frac{1}{8}$ accompanied by high resistivity. At nearby concentrations one might expect the system to phase separate into the ordered $x = \frac{1}{8}$ phase, or, more likely, defects will apear in the ordered phase as in other commensurate to incommensurate transitions.

Turning from these more global signatures of charge localization and ordering, and their coupling to spin and lattice, it is especially exciting that **local** probes are now beginning to yield direct information on polaron formation and ordering. Early XAFS measurements [34] clearly demonstrated that the $Mn\,O$ distances developed multiple length-scales above T_{MI} consistent with small polaron formation in a homogeneous background matrix. Careful neutron PDF measurements [32] in $La_{1-x}Ca_xMn\,O_3$ ($x = 0.12, 0.21, 0.25$) have supported and significantly expanded this result. Billinge et al [32] found a large change in the local structure connected with the metal–insulator transition for $x = 0.21, 0.25$ (and no such change in the $x = 0.12$ sample which exhibits no metal–insulator transition). The local structure change is plausibly modeled as an isotropic collapse of oxygens toward the Mn of magnitude $\delta = 0.12A$ occuring on one in four Mn sites. Importantly, these authors also find a large ($\Delta T \approx 50K$) temperature range **below** T_{MI} where strongly non–thermal $Mn\,O$ distortions persist, indicative of precursor fine–scale lattice distortions. Similar anomalous deviations from harmonic Debye–Waller behaviour were also observed in $La_{0.65}Ca_{0.35}Mn\,O_3$ by a careful reanalysis (following the increasing evidence for unusual lattice effects) of powder neutron studies [31]. The evidence for local structural defects is further illuminated by the neutron PDF work of Louca et al [33] on $La_{1-x}Sr_xMn\,O_3$ ($x = 0 - 0.4$). These authors demonstrate that the local atomic structure deviates from the average crystallographic structure throughout this x–range, including both the orthorhombic and rhombohedral crystal structures; the crystallographic rhombohedral structure shows no signatures of distortions of $Mn\,O_6$ octahedra, see Fig. 2. The PDF signatures for local Jahn–Teller distortions occur as small (hole) polarons in the in the paramagnetic insulating phase and persist as local (but more extended) polaron distortions below the transition in the ferromagnetic metallic phase, resulting in percolative and

inhomogeneous metal signatures for transport and magnetic properties.

The notion of **local** JT distortions even in the rhombohedral and metallic phases is entirely consistent with the angle–resolved photoemission and XAS park et al reports of [36], and with the large isotope ($^{16}O/^{18}O$) dependence of T_c [37].

Finally we note the exciting beginning of direct HREM imaging of lattice distortions in microdomains of charge localized carriers. Hervieu et al [39] have studied $Pr_{0.7}\,Ca_{0.25}Sr_{0.05}Mn\,O_3$ and $Pr_{0.75}\,Sr_{0.25}Mn\,O_3$ and been able to directly image monoclinic domains in a $Gd\,Fe\,O_3$–type background matrix . They suggest strong local modifications of the $Mn\,O_6$ octahedral structure around localized charges (Mn^{4+}). These localized lattice and charge distortions are observed to cluster into microdomains of short linear segments which may be viewed as $(A^{2+}Mn^{4+}O_3)_n$ embedded in the mixed valent Mn^{3+}–Mn^{4+} perovskite matrix. Presumably these microdomains will order into charge–ordered superlattice phases near commensurate dopings.

Theoretical approaches:

As pointed out above initially theoretical investigations focused on the study of the DE mechanism. The early mean–field theories [3, 6, 7] and even the $d = \infty$ mean–field theory of Furukawa [9] all describe the FMM as a simple ferromagnet, and the conduction as that of a simple metal. However, as early as 1982 Kubo [52] pointed out that the problem is not that simple. From exact diagonalization in a one dimensional model he noticed that even the ground state of the ferromagnetic Kondo lattice (FKLM) may be unusual (for periodic boundary conditions). He also points out that even if there is a simple ferromagnetic ground state, there are other states closeby in energy, which would give rise to unconventional excitations. This work was extended by Zang et al [53], in which small 2 and 3 dimensional systems , and their excitations were studied in detail. It was found that only for very special concentrations is a simple ferromagnet indeed the groundstate of this model. Th excitation spectrum of the KLM model shows atypical spin–wave disperions for large wave vectors. This new and unusual excitations are born out experimentally in the unusual spin dynamics seen the μSR experiments by Heffner et al [35], and by the surprising incoherent spin wave scattering observed by Lynn et al [54]. The μSR experiments [35] show clearly that there are slow spatially inhomogeneous spin dynamics below T_c. However, there is substantial experimental controversy; e.g. Perring et al. [55] find perfect agreement of the spin wave dispersion of a simple nearest neighbour ferromagnetic Heisenberg model with their neutron scattering data. In light of the importance of local effects on structure and transport, it would be extremely desirable to have similar data for spin structures, for example via spin–polarized neutron PDF. Being faced with the problem that all approximate treatments of the FKLM are inconclusive Röder et al [56] performed a high temperature series analysis of the FKLM. This analysis clearly shows a transition at the experimentally observed values. However, the concentration dependence of this transition resembles the one obtained for a ferromagnetic ferrimagnet. This might explain the perfect spin–wave disperion observed by Perring et al. [55], since the lower branch of a ferrimagnets dispersion is exactly like the one of a nearest neighbour Heisenberg model. In addition, a ferrimagnetic ordering would imply a tendency of the purely electronic FKLM towards charge ordering and charge localization. This pre–formation of charge-ordering renders the FKLM very susceptible to the formation of ordered polaron states, when lattice effects are included.

Notwithstanding the theoretical difficulties arising from the complicated many–body effects of the FKLM Kondo lattice model, a coupling of charge and lattice

degrees of freedom is necessary both on theoretical and experimental grounds. In a theoretical treatment one necessarily has to resort to various mean–field theories.

In a dynamic mean–field theory Millis et al [18, 19] treat the DE coupling dynamically, but use the frozen–phonon approach for the lattice. Due to pecularities of the dynamic mean–field theory ($d = \infty$) they only treat extreme densities $x = 0$ and $x = 1$. As a result of this calculation they observe a metal–insulator transition driven by the localization of electrons on disorder induced by lattice–fluctuations. They mimic the x–dependence by a variation in the strength of the Jahn–Teller (electron–phonon) coupling constant. Unfortunately this description does not allow the inclusion of local structure effects due to the limitations of the dynamic mean–field theory.

Th approach taken by Röder et al [16, 17] is in some sense complementary, since it uses standard mean–field theory for the DE coupling. This assumes that the electrons move in a static field created by the spin (this approximation is correct in the classical limit), but allowing for phonon dynamics by using a well–established variational scheme. Their results agree qualitatively with the ones by Millis et al., but allow a more systematic study of the concentration dependence. It should be possible to actually use the treatment of the phonons from [16, 17] in the ($d = \infty$) theory, and also to extent the calculation of [18, 19] for more realistic fillings. Such a theory would show the dependenc of the tranition on the various time scales arising from charge, spin and lattice degrees of freedom.

Unfortunately, if one is interested in local structure effects, it is necessary to resort to the approximations in [16, 17]. As pointed out before such an unrestricted – in the sense that we allow the field variables to be spatially inhomogeneous – calculation explicitly shows the temperature dependence of the spatial of the various fields involved. This question is especially interesting closely above T_c. The coupling of the lattice polarons to the magnetic degrees of freedom via the DE interaction leads to the phenomena of entropic localization. Magnetoelastic polarons consist of a fairly localized lattice distortion, a localized charge and a ferromagnetic bubble which extends from the center of the polaron over the neigbouring sites. As the temperature increases the entropy in the disordered spin background becomes more important and compresses the ferromagnetic bubble, leading to an increasing localization with temperature. This picture is a single particle description and needs to be modified if the density of polarons becomes large. In perliminary studies we have investigated the interaction of two such magnetoelastic polarons ,see Figs. 2,3. As the temperature is lowered at high temperature localized polarons interact via their magnetic part, wich is of longer range than either their lattice or charge constituents, and form a variety of bound states with ever–increasing equilibrium radius. Within these large bound multipolarons first spin and then charge decouple from the lattice degrees of freedom, which might eventually lead to the breakdown of the magnetoelastic polaron below the transition. These studies need to be extended in various directions.

For the explanation of the measured isotope effect [37] it is necessary to remain in a two–orbital description. If one wants to project onto a single orbital description it is necessary to resort to phenomenological changes in the electron phonon coupling constant with isotopic substitution. In the two–orbital description this effect is more transparent.

The nature of the lattice distortion arises from two sources. As pointed out by Millis [57] in addition to Jahn–Teller distortions caused by the splitting of the occupied e_g–levels in a cubic field, induced holes would lead to breathing like distortions which would frustrate the Jahn–Teller ordering. This may give rise to an order–disorder transition involving the Jahn–Teller distorted octahedra. It is important to include the relative dynamics betweeen the various lattice modes; the breathing modes may not

to a localization at all, depending on how slow or fast the respective lattice relaxations are. This physics may be included using the microscopic interaction Hamiltonian in [57] and the unrestricted mean field approach from [56]. However, even more important may be static disorder induced by the distribution of cations of different radii, as first pointed out in [47]. If there are both frustration and disorder present one might expect glasssy behaviour with respect to local modes, and not caused by frustrated spin interactions, as in spin glasses. Such lattice glas models may hinder the freezing of the lattice in commensurate and therefore charge ordered states and lead eventually to the charge delocalization as in the FMM phase.

It is important to note that the scattering of the electrons on spin disorder in the paramagnetic phase does not lead to a localization of the electron wave function at realistic concentrations [58]. Therefore Anderson localization cannot explain the observed activated behavior above T_c.

Future directions

As in other transition metal perovskites, the CMR manganite oxides represent a class of complex electronic materials where strong coupling of spin, charge and lattice degrees–of–freedom is the essential ingredient. These microscopic couplings, together with disorder (e.g. from dopant ions), result in competing interactions (disorder plus frustration) which drive multiscale textures and associated (glassy) dynamics. The macroscopic functionalities (CMR, ferroelectric, superconducting, etc.) are determined by this mesoscale complexity. Thus understanding the microscopic–mesoscopic–macroscopic relationships will be a prevailing research theme in these and other complex electronic materials, as a route to providing scientific principles for controlling synthesis–structure–property relationships.

We have emphasized that if this strategy is to yield a validated and predictive modeling capability, it will require **correlated** probing of spin, charge and lattice properties on multiple length and timescales, including local scales. The complexity manifests itself as fine–scale structure (twinning, tweed, microdomains) and elasticity in materials science, but as charge localization and ordering (polarization, polaron formation, and superlattices) in solid state physics. Correspondingly, modeling must focus on minimal models which respect spin, charge and lattice, and incorporate distinctly nonlinear, nonadiabatic, and discrete lattice effects. As we have emphasized, both experiment and theory are now faciliatating this agenda, and this will surely mark future research on CMR in manganite oxides and related materials. The materials, their intriguing functionality (CMR), and new experimental and theoretical techniques have converged fortuitously to make this an exciting new era for studying small polaron physics – in the generalized coupled spin, charge, lattice sense we have discussed here – and the intrinsic fine scale structure associated with solid–solid (elastic) phase transformations. This synergy of solid state physics and materials science perspectives holds rich promise.

The issue of time scales is worth emphasizing. This has long been a fundamental concern for fine–scale precursor structure at solid–state phase transformations, especially of elastic, martensitic character. Is the JT distortion static or dynamic or both? Are their cluster dynamic time scales giving rise to central peaks in the dynamic structure factor? What is the dynamics of nucleation? Controversies surrounding these questions have a confusing history (see e.g. [59, 60] and references therein), because time scale probes have been very limited. The expectation of multiple spatial scales for the mesoscopic octahedral distortions in fact leads to expectations of multiple

temporal scales, of even hierarchical or glassy character There are some preliminary suggestions of such glassy responses in recent μSR data [35], as well as controversial neutron dynamics results (see above) [31, 32]. This certainly will be another focal area for future experimental research.

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Figure 1: A sketch of the phasediagram of the CMR materials. The lines are only guides to the eye. The various phases are: paramgnetic insulators (PMI), antiferromagnetic insulators (AFI), ferromagnetic metal (FMM), antiferromagnets (AF), and charge–ordered (CO).

Figure 2: The Mn–O bondlengths as determined from the the PDF (triangles) compared to those deduced from the lattice constants of the crystal structure (solid lines L, S1 and S2). Note that the local distortion is present even in the rhombohedral phase. From [33].

Figure 3: The charge (a.) and spin (f.) configuration of two interacting magnetoelastic polarons. The picture is a cross section from a 30^3 system with periodic boundaries. The greyscale indicates the charge and spin distribution, respectively. Note that the charge is more localized than the spin.